

### REMARKS

The Office Action dated October 13, 2005 has been carefully reviewed. Claims 1-7 and 13-25 are pending in the application. Claims 8-12 and 26-32 have been canceled without prejudice to Applicant's right to file one or more divisional applications directed thereto. Applicant requests reconsideration of the rejection of Claims 1-7 and 13-25 is respectfully requested as well as allowance of the claims on the basis of the following remarks.

#### Summary of the Invention

The present invention provides a method for the resisting corrosion of metal elements in concrete. Sequestration of chloride ions and/or nitrite release is provided for by the disclosed and claimed method. The sequestration and/or nitrite release oxidizes the metal to form a protective barrier on the surface to further reinforce the concrete.

#### Independent Claims 1 and 13

Independent claim 1 recites a method of resisting corrosion of metals in concrete, wherein at least one chloride-sequestering compound having the formula  $3\text{Me(II)O}\cdot(\text{R}, \text{R}')_2\text{O}_3\cdot\text{Me(II)(anion)}_2\cdot n\text{H}_2\text{O}$  is introduced into concrete. Specifically, R and R' are different elements and are independently selected from the group consisting of Al, Fe, and Cr. The anion ("anion") is selected from the group consisting of  $\text{NO}_2$ ,  $\text{NO}_3$ , and OH, wherein n is a value ranging from 0 to 24. Me(II) is a cation which is selected from the group consisting of Ca, Ba, Sr, Mn, Zn, and combinations thereof.

Independent claim 13 recites a method of resisting corrosion of metals in a concrete structure, creating an overlay containing at least one chloride-sequestering combination compound having the formula  $3\text{Me(II)O}\cdot(\text{R}, \text{R}')_2\text{O}_3\cdot\text{Me(II)(anion)}_2\cdot n\text{H}_2\text{O}$ , wherein the overlay is secured adjacent to the concrete structure and the sequestering chloride ions in the overlay. Specifically, R and R' are different elements and are independently selected from the group consisting of Al, Fe, and Cr. The anion ("anion") is selected from the group consisting of  $\text{NO}_2$ ,  $\text{NO}_3$ , and OH, wherein n is a value ranging from 0 to 24. Me(II) is a cation which is selected from the group consisting of Ca, Ba, Sr, Mn, Zn, and combinations thereof.

Response to Restriction Requirement

Applicant hereby reaffirms the election to pursue Claims 1-7 and 13-25. Please cancel Claims 8-12 and 26-32 without prejudice to Applicant's right to file one or more divisional applications directed thereto.

35 U.S.C. § 103 (a) Obviousness Rejections

Claims 1-7 and 13-25 have been rejected under 35 U.S.C. § 103(a) as being obvious in view of U.S. Patent No. 5,435,846 to Tatematsu et al. ("Tatematsu"); the abstract of Ratinov et al., "Inhibitors of corrosion of the reinforcement steel in concrete with addition of calcium chloride," Tr. Nachn.-Issled. Inst. Betona I Zhelezobetona, No. 22, 40-53 (1961) ("Ratinov"); or U.S. Patent No. 5,356,472 to Odler ("Odler"); alone or in view of U.S. Patent No. 4,285,733 to Rosenberg et al. ("Rosenberg '733") or U.S. Patent No. 4,092,109 to Rosenberg et al. ("Rosenberg '109"). Applicant respectfully traverses the § 103(a) rejection with respect to Claims 1-7 and 13-25. The Examiner cites to Tatematsu which teaches a hydrocalumite additive ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{NO}_2)_2 \cdot n\text{H}_2\text{O}$ ) on numbered pages 2 to 3 of the Office Action.

The Examiner is also correct in stating, on numbered Pages 2 to 3 of the Office Action, that the Tatematsu hydrocalumite additive is described on Page 8 of Applicant's specification. However, while this additive is disclosed, it is *not expressly claimed*. Moreover, Claims 1-7 and 13-25, which are currently pending, are directed to a method which entails the use of a combination compound with the following formula:  $3\text{Me(II)O} \cdot (\text{R}, \text{R}')_2\text{O}_3 \cdot \text{Me(II)(anion)}_2 \cdot n\text{H}_2\text{O}$ , where R and R' are different and are independently selected from the group consisting of Al, Fe, and Cr. Accordingly, Applicant's *disclosed and claimed* combination compound,  $3\text{Me(II)O} \cdot (\text{R}, \text{R}')_2\text{O}_3 \cdot \text{Me(II)(anion)}_2 \cdot n\text{H}_2\text{O}$  (which is expressly recited in claims 1, 7, and 13), is distinct from the Tatematsu hydrocalumite additive,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{NO}_2)_2 \cdot n\text{H}_2\text{O}$ . Further, dependent claims 2-6 depend from claim 1 and dependent claims 14-25 depend from claim 13, thereby incorporating this claim limitation. Accordingly, Claims 1-7 and 13-25 all, directly or indirectly, recite a combination compound,  $3\text{Me(II)O} \cdot (\text{R}, \text{R}')_2\text{O}_3 \cdot \text{Me(II)(anion)}_2 \cdot n\text{H}_2\text{O}$ , which is separate and distinct from the Tatematsu hydrocalumite additive,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{NO}_2)_2 \cdot n\text{H}_2\text{O}$ .

The Examiner further acknowledges the distinction between Applicant's combination additive and the Tatematsu hydrocalumite, but theorizes, without reference to any scientific source, on numbered page 3 of the Office Action that "ion exchange" can occur such that the alumina in the Tatematsu hydrocalumite and iron oxide form Applicant's above-referenced combination additive of iron oxide and alumina. (While the Examiner refers to " $2\text{CaO} \cdot \text{Fe}_{(2-x)}\text{Al}_x\text{O}_3 + a\text{CaO}$ " as Applicant's claimed combination additive on numbered Page 3 of the Office Action, Applicant respectfully clarifies that, while this is disclosed in the specification, it is not expressly claimed. Applicant assumes that the Examiner intended, instead, to direct his discussion in view of the following compound,  $3\text{Me(II)O} \cdot (\text{R}, \text{R}')_2\text{O}_3 \cdot \text{Me(II)(anion)}_2 \cdot n\text{H}_2\text{O}$ , which is recited in Claims 1-7 and 13-25.)

Contrary to the Examiner's contention, however, iron compounds, *including* iron oxide, are normally unreactive in concrete due to the ambient pH values present in concrete which render the iron oxide highly insoluble; therefore, ion exchange cannot occur under normal conditions, as one of ordinary skill in the art would know that ions have to have at least moderate solubilities in order for the ion exchange process to occur *in situ*. Moreover, there is no evidence that the iron oxide that normally forms during the corrosion of embedded steel in concrete is actually "consumed" chemically so as to form other derivative compounds *in situ*. Further, Applicant's sequestration method does *not* involve ion exchange of iron oxide and aluminum, nor does Tatematsu disclose or claim Applicant's sequestration method, or any similar variation thereof.

Moreover, the existence of an aluminum-containing compound, such as Tatematsu's compound, does not imply the existence of an analogous iron or iron-aluminum containing compound. As one ordinarily skilled in the art would appreciate, different elements such as iron and aluminum have varying degrees of reactivity due to their different chemical and physical properties, including molecular orbital configuration and the unique chemical and physical interaction which occurs when reacting with other elements.

Also, one ordinarily skilled in the art would not have the teaching, motivation, or suggestion to even devise a synthetic method for an iron-aluminum sequestration additive as disclosed claimed by Applicant. Simply put, there is no teaching, motivation, or suggestion in the cement art, based upon the literature or standard texts, which indicate

that incorporating iron in any way, shape, or form would enhance reactivity of any compound normally found in concrete. Therefore, such a method for making an *iron-aluminum compound* would not appear to be a viable option for one seeking to synthesize or even use a chloride sequestration additive in concrete to one ordinarily skilled in the art.

Accordingly, to also address Examiner's second point with regard to Tatematsu on numbered Page 3 of the Office Action, an unexpected result is disclosed and claimed in the instant application because one ordinarily skilled in the art would not anticipate the Applicant's additive to be reactive and therefore such an iron-aluminum containing compound would most likely not be used as a method for sequestering chloride ions.

Also, with regard to additional distinctions vis-à-vis Tatematsu, Applicant's method for sequestering chloride ions, as recited in Claim 1, is as follows: a method of resisting corrosion of metals in concrete, wherein at least one chloride-sequestering compound having the formula  $3\text{Me(II)O}\cdot(\text{R}, \text{R}')_2\text{O}_3\cdot\text{Me(II)(anion)}_2\cdot n\text{H}_2\text{O}$  is introduced into concrete. Specifically, R and R' are different elements and are independently selected from the group consisting of Al, Fe, and Cr. The anion is selected from the group consisting of  $\text{NO}_2$ ,  $\text{NO}_3$ , and OH, wherein n is a value ranging from 0 to 24. Me(II) is a cation which is selected from the group consisting of Ca, Ba, Sr, Mn, Zn, and combinations thereof.

Further distinctions from Tatematsu include the following dependent claims which depend from independent method Claim 1 for chloride sequestration, including the following:

a) chloride sequestration results in a chloride-containing compound having a low solubility in concrete (Claim 2);

b) the cation is Ca, R is Al and R' is Fe (Claim 3);

c) the concrete is fresh concrete and said compound is introduced in an amount of about 3 to 88 pounds of particulate solid per cubic yard of hydrated fresh concrete (Claim 4);

d) R and R' are derived from solid sources (Claim 5);

e) the ratio of R to R' is about 1:1 (Claim 6); and,

f) a reaction,  $3\text{Me(II)O}\cdot(\text{R}, \text{R}')_2\text{O}_3\cdot\text{Me(II)(NO}_2)_2\cdot n\text{H}_2\text{O} + 2\text{Cl}^- \rightarrow 3\text{Me(II)O}\cdot(\text{R}, \text{R}')_2\text{O}_3\cdot\text{Me(II)Cl}_2\cdot n\text{H}_2\text{O} + 2\text{NO}_2^-$ , creates the chloride-sequestering compound and established the corrosion resistant oxide layer (Claim 7).

Further distinctions from Tatematsu include the following dependent claims which depend from independent method Claim 13 for chloride sequestration, including the following:

- a) the overlay is created on the concrete structure (Claim 14);
  - b) the overlay is preformed and then secured to the concrete structure (Claim 15);
  - c) the preformed overlay is secured to the concrete structure by adhesive (Claim 16);
  - d) applying the overlay to the concrete structure as a slurry (Claim 17);
  - e) applying a second layer over the slurry overlay (Claim 18);
  - f) providing the second layer with lower porosity than the slurry overlay (Claim 19);
  - g) employing a material selected from the group consisting of concrete, asphalt, Portland cement, clay, calcium aluminate cement, and mortar in the overlay (Claim 20);
  - h) introducing high ionic strength liquid into the overlay (Claim 21);
  - i) employing the method in a concrete structure disposed at least partially under water (Claim 22);
  - j) performing the method without requiring ongoing input of electrical energy (Claim 23);
  - k) establishing the overlay with a thickness of about 0.5 to 10 inches (Claim 24);
- and,
- l) establishing the overlay with a thickness of about 1 to 4 inches (Claim 25).

Therefore, in view of the foregoing, Applicant respectfully submits that Claims 1-7 and 13-25, as also described above, are not obvious in view of Tatematsu, as Examiner's unsupported contention that "ion exchange" *can* occur between alumina in the Tatematsu hydrocalumite additive and iron oxide to form the Applicant's combination additive.

The Examiner cites to Ratinov et al. (abstract), "Inhibitors of corrosion of the reinforcement steel in concrete with addition of calcium chloride," Tr. Nauchn-Issled Inst Betona I Zhelezobetona (1961), No. 22, p. 40-53, on numbered Page 3 of the Office Action, which teaches a corrosion inhibitor comprising calcium chloride and sodium nitrite used to form a calcium hydronitro-aluminate. The Examiner further theorizes, without citing to any scientific source, that "ion exchange" can occur between alumina in the Ratinov hydronitro-aluminate additive and iron oxide to form the Applicant's

combination additive of iron oxide and alumina. (While the Examiner refers to “ $2\text{CaO}\cdot\text{Fe}_{(2-x)}\text{Al}_x\text{O}_3 + a\text{CaO}$ ” as Applicant’s claimed combination additive on numbered Page 3 of the Office Action, Applicant respectfully clarifies that, while this is disclosed in the specification, it is not expressly claimed. Applicant assumes that the Examiner intended, instead, to direct his discussion in view of the following compound,  $3\text{Me(II)O}\cdot(\text{R}, \text{R}')_2\text{O}_3\cdot\text{Me(II)(anion)}_2\cdot n\text{H}_2\text{O}$ , which is recited in Claims 1-7 and 13-25.)

However, iron oxide is normally unreactive in concrete due to the ambient pH values present in concrete which render the iron oxide highly insoluble; therefore, ion exchange cannot occur under normal conditions, as one of ordinary skill in the art would know that ions have to have at least moderate solubilities in order for the ion exchange process to occur *in situ*. Furthermore, the sequestration method of the present application does not involve such ion exchange of Fe for Al or  $\text{Fe}_2\text{O}_3$  for  $\text{Al}_2\text{O}_3$ .

Further, the existence of an aluminum-containing compound, such as Ratinov’s compound, does not imply the existence of an analogous iron or iron-aluminum containing compound. As one ordinarily skilled in the art would appreciate, different elements such as iron and aluminum have varying degrees of reactivity due to their different chemical and physical properties, including molecular orbital configuration and the unique chemical and physical interaction which occurs when reacting with other elements. Moreover, there is no evidence that the iron oxide that normally forms during the corrosion of embedded steel in concrete is actually “consumed” chemically so as to form other derivative compounds *in situ*. Further, Applicant’s sequestration method does *not* involve ion exchange of iron and aluminum or their oxides, nor does Ratinov disclose or claim Applicant’s sequestration method, or any similar variation thereof.

Moreover, one ordinarily skilled in the art would not have the teaching, motivation, or suggestion to even devise a synthetic method for using an iron-aluminum containing sequestration additive, as disclosed and claimed by Applicant. Simply put, there is no teaching, motivation, or suggestion in the cement art, based upon the literature or standard texts, which indicate that incorporating iron in any way, shape, or form would enhance reactivity of any compound normally found in concrete. Accordingly, such an iron-aluminum additive would not appear to be a viable option for one seeking to synthesize or even use a chloride sequestration additive in concrete to one ordinarily skilled in the art.

With regard to distinctions as recited in Applicant's claims with regard to the Ratinov reference, the discussion of Applicant's method as set forth at **Page 8 to Page 9** in connection with Tatematsu is equally applicable here.

Therefore, in view of the foregoing, Applicant respectfully submits that Claims 1-7 and 13-25 are not obvious in view of Ratinov, as Examiner's unsupported contention that "ion exchange" *can* occur between alumina in the Ratinov corrosion inhibitor and iron oxide to form the Applicant's combination additive, as described above.

Moreover, the existence of an aluminum-containing compound, such as  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4$  as described in Odler, does not imply the existence of an analogous iron or iron-aluminum containing compound. In fact, no iron-containing analog of this compound exists. Moreover, there is no evidence that the iron oxide that normally forms during the corrosion of embedded steel in concrete is actually "consumed" chemically so as to form other derivative compounds *in situ*. Further, Applicant's sequestration method does *not* involve ion exchange of iron oxide and aluminum, nor does Odler disclose or claim Applicant's sequestration method, or any similar variation thereof.

Further, while Odler does describe the "ferrite" phase which forms  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ , as is well accepted in the scientific literature and which is established by the Bogue calculation (and widely accepted in the cement industry) (please refer to pages 62 and 63 from Taylor: Cement Chemistry, enclosed herewith), Applicant does not claim  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ . Rather, the range of compositions as claimed by Applicant have Fe/Al ratios in excess of 1 and these compositions do not form intrinsically in cement, as cement is formulated to avoid their formation. As one ordinarily skilled in the art would appreciate, different elements such as iron and aluminum have varying degrees of reactivity due to their different chemical and physical properties, including molecular orbital configuration and the unique chemical and physical interaction which occurs when reacting with other elements.

Moreover, one ordinarily skilled in the art would not have the teaching, motivation, or suggestion to even devise a synthetic route for an iron-aluminum containing sequestration additive. Simply put, there is no teaching, motivation, or suggestion in the cement art, based upon the literature or standard texts, which indicate that incorporating iron in any way, shape, or form would enhance reactivity of any compound normally found in concrete. Accordingly, such an iron-aluminum additive would not appear to be a

viable option for one seeking to synthesize or even use a chloride sequestration additive in concrete to one ordinarily skilled in the art. Therefore, the presently invented iron-aluminum containing sequestering additive, which naturally would have to be reactive with chloride ions for the sequestration to occur, would not be expected to one ordinarily skilled in the art to yield such chloride sequestration activity.

With regard to distinctions as recited in Applicant's claims with regard to the Odler reference, the discussion of Applicant's method as set forth at **Page 8 to Page 9** in connection with Tatematsu are equally applicable here.

Therefore, in view of the foregoing, Applicant respectfully submits that Claims 1-7 and 13-25, as also described above, are not obvious in view of Odler, as Odler only teaches that  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  is naturally formed in cement, but not Applicant's additives; moreover, one ordinarily skilled in the art would not expect that Applicant's additives would naturally form in cement on account of the Bogue calculation, as referenced above, and which is widely accepted in the cement industry.

The Examiner cites to the Rosenberg references ('109 and '733 patents) on numbered Page 4 of the Office Action which teach that it is old in the art to add nitrites to prevent corrosion and that it is understood that the addition of nitrites or nitrates assist in the formation of an iron oxide protective coating of the metal article to be protected.

The Examiner acknowledges that Rosenberg is old in the art on numbered Page 4 of the Office Action. More specifically, these Rosenberg references teach the addition of calcium nitrite to reinforce steel-embedded concrete which forms a protective iron oxide coating – a physical barrier which impedes the access of chloride ions to the steel. However, as distinguished from Applicant's invention, there is no chloride sequestration which is taught or suggested in the Rosenberg references. The method of chloride sequestration, as disclosed and claimed in the present invention, helps to further resist corrosion by sequestering the chloride ions. However, the Rosenberg references teach the use of nitrites which are not effective until corrosion of the embedded-steel concrete actually occurs.

Also, the Rosenberg references do not teach either the method of direct chloride sequestration (as disclosed and claimed by Applicant) or ion exchange (to address Examiner's point regarding the same). Rather, these references merely teach the rapid oxidation of Fe(II) to Fe(III) with the objective of producing a physical barrier of iron(III)



oxide/hydroxide at the surface of the corroding, reinforcing steel. This physical barrier is intended to physically impede the access of the chloride ions to the reinforcing steel.

The Examiner also further implies on numbered Page 4 of the Office Action, without citing to any scientific source, that “ion exchange” can occur between alumina, calcium oxide, as disclosed in the above-discussed primary references (Tatematsu, Ratinov, Odler), iron oxide, and the nitrites, as taught by the Rosenberg references, to form the Applicant’s combination additive. Contrary to the Examiner’s contention, however, iron oxide is normally unreactive in concrete (*including*, but not limited to, Portland cement) due to the ambient pH values present in concrete which render the iron oxide highly insoluble; therefore, ion exchange cannot occur under normal conditions, as one of ordinary skill in the art would know that ions have to have at least moderate solubilities in order for the ion exchange process to occur *in situ*. Moreover, there is no evidence that the iron oxide that normally forms during the corrosion of embedded steel in concrete is actually “consumed” chemically so as to form other derivative compounds *in situ*. Further, Applicant’s sequestration method does *not* involve ion exchange of iron oxide and aluminum, nor does either Rosenberg reference or even the primary references (i.e., Tatematsu, Ratinov, and Odler) in view of either Rosenberg reference, disclose or claim Applicant’s sequestration method, or any similar variation thereof.

Further, the existence of an aluminum-containing compounds, such as Tatematsu’s ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_2)_2\cdot n\text{H}_2\text{O}$ ), Odler’s ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4$ ), or Ratinov’s (calcium hydronitro-aluminate) compounds, as described above, even in combination with the nitrites as taught in Rosenberg, do not imply the existence of analogous iron or iron-aluminum containing compounds. As one ordinarily skilled in the art would appreciate, different elements such as iron and aluminum have varying degrees of reactivity due to their different chemical and physical properties, including molecular orbital configuration and the unique chemical and physical interaction which occurs when reacting with other elements.

Moreover, one ordinarily skilled in the art would not have the teaching, motivation, or suggestion to even devise a synthetic method for an iron-aluminum containing sequestration additive, such as the method for using such an additive as disclosed and claimed by Applicant. Simply put, there is no teaching, motivation, or suggestion in the cement art, based upon the literature or standard texts, which indicate that incorporating

iron in any way, shape, or form would enhance reactivity of any compound normally found in concrete. Accordingly, such an iron-aluminum additive would not appear to be a viable option for one seeking to synthesize or even use a chloride sequestration additive in concrete to one ordinarily skilled in the art. Therefore, the presently invented iron-aluminum containing sequestering additive, which naturally would have to be reactive with chloride ions for the sequestration to occur, would not be expected to one ordinarily skilled in the art to yield such chloride sequestration activity.

Further, there is no suggestion in either of the Rosenberg references for combining those references with the primary references (i.e., Tatematsu, Ratinov, and Odler) as relied upon the Examiner. As stated in In re Imperato, 179 USPQ 730 (CCPA 1973) at 732:

With regard to the principal rejection, we agree that combining the teaching of Schaefer with that of Johnson or Amberg would give the beneficial result observed by appellant. However, the mere fact that those disclosures can be combined does not make the combination obvious unless the art also contains something to suggest the desirability of the combination.... We find no such suggestion in these references.

Also, with regard to distinctions as recited in Applicant's claims with regard to the Rosenberg references and also the primary references (i.e., Tatematsu, Odler, and Ratinov), the discussion of Applicant's method as set forth at **Page 8 to Page 9** in connection with Tatematsu is equally applicable here.

Therefore, in view of the foregoing, Applicant respectfully submits that Claims 1-7 and 13-25 are not obvious in view of the Rosenberg references (and even these references in view of Tatematsu, Ratinov, and Odler) for the reasons as described above.

#### Double Patenting Rejections

Claims 1-7 and 13-25 are rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over Claims 1-21, 1-33, and 1-12 of U.S. Patent Nos. 6,610,138, 6,810,634, and 6,755,925 to Brown, respectively. In addition, Claims 1-7 and 13-25 are provisionally rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over Claims 1-42 of co-pending U.S. Patent Application No. 11/078,170 to Brown, and Claims 1-8 of co-pending U.S. Patent Application No. 11/039,101 to Brown. Applicant submits herewith a

terminal disclaimer over U.S. Patent Nos. 6,610,138, 6,810,634, and 6,755,925, and U.S. Patent Application Nos. 11/078,170 and 11/039,101, which should obviate the double patenting rejection.

Summary

In view of the foregoing amendments and remarks, Claims 1-7 and 13-25 are believed to be in allowable form. Applicant respectfully requests allowance of the application.

In the event that any outstanding matters remain in connection with this application, the Examiner is invited to telephone the undersigned at 412-566-5907.

Respectfully submitted,



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# Cement Chemistry

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$$C_3S = 4.0710CaO - 7.6024SiO_2 - 6.7187Al_2O_3 - 1.4297Fe_2O_3 \quad (3.4)$$

$$C_2S = -3.0710CaO + 8.6024SiO_2 + 5.0683Al_2O_3 + 1.0785Fe_2O_3 \\ = 2.8675SiO_2 - 0.7544C_3S \quad (3.5)$$

$$C_3A = 2.6504Al_2O_3 - 1.6920Fe_2O_3 \quad (3.6)$$

$$C_4AF = 3.0432Fe_2O_3 \quad (3.7)$$

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As with LSF, the approach is applicable to cements if CaO is further corrected by deducting 0.7SO<sub>3</sub>. Because minor oxide components are ignored, the total for the four main phases plus free lime will not add up to 100%. It is implicit in the approach that all the MgO is assumed to occur as periclase. The phase composition calculated by Bogue's method is related to the LSF in that a ratio of C<sub>2</sub>S to C<sub>3</sub>A ≤ 0.546, calculated without correcting the CaO content for free lime, corresponds to an LSF ≥ 1.0 (D2).

The results of the Bogue calculation are often called potential phase compositions, because when the procedure was devised, it was generally considered that the principal source of error was failure to reach equilibrium during cooling. The results do indeed differ, probably often markedly, from the true phase compositions, notably in underestimating alite and overestimating belite (Section 4.4.6), and it is unlikely that equilibrium is maintained during cooling, but the direct source of error is that the compositions of the clinker phases differ considerably from those of the pure compounds. Bogue compositions are used in some specifications, and for proportioning by setting up and solving equations to calculate the relative amounts of raw materials needed to obtain given 'potential' contents of C<sub>3</sub>S or other phases. They have often been misused for other purposes on the assumption that they are close to the actual phase compositions. Spohn *et al.* (S19) have indicated the dangers of such uncritical use.

#### 3.1.4 Enthalpy changes in clinker formation

The enthalpy change on formation of Portland cement clinker cannot be calculated with high precision, mainly because of uncertainties associated with the clay minerals in the raw material. Table 3.1 gives data for the main thermochemical components of the reaction, almost all of which have been calculated from a self-consistent set of standard enthalpies of formation, and which are therefore likely to be more reliable than other values in the literature. The conversion of the clay minerals into oxides is an imaginary reaction, but valid as a component in a Hess's law calculation. Few reliable thermochemical data exist for clay minerals; those for pyrophyllite and kaolinite can probably be used with sufficient accuracy, on a weight basis,

function to LSF are used in some countries. A suggested modification to the LSF definition, intended to allow for magnesium substitution in alite, replaces  $\text{CaO}$  by  $(\text{CaO} + 0.75\text{MgO})$  for  $\text{MgO} \leq 2\%$ , or by  $(\text{CaO} + 1.5)$  for  $\text{MgO} > 2\%$  (S19). In the German literature, Kalkstandard II corresponds approximately to LSF and Kalkstandard III to this modification of it.

The SR and AR, also respectively called silica modulus and alumina modulus, are empirically based. For normal types of Portland cement clinker, SR is usually 2.0–3.0, and AR 1.0–4.0, but these ranges do not apply to special types, such as sulphate-resisting or white cement clinkers. The SR governs the proportion of silicate phases in the clinker. Increase in SR lowers the proportion of liquid at any given temperature in the kiln, and thus makes the clinker more difficult to burn. The AR governs the ratio of aluminate to ferrite phases in the clinker, which has important effects on cement properties, and also determines the quantity of liquid formed at relatively low temperatures; at  $1338^\circ\text{C}$ . for a given total content of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , the quantity of liquid theoretically passes through a maximum at an AR of 1.38.

The proportions of raw materials are commonly calculated on the basis of the above parameters, most obviously by setting up and solving simultaneous equations; to fix  $n$  parameters,  $n + 1$  raw materials of appropriate composition are required. It is also necessary to consider the desired or allowable contents of minor components.

### 3.1.3 The Bogue calculation

In another approach, widely used in the USA and elsewhere, the quantitative phase composition is estimated using a procedure due to Bogue (B24). It is necessary also to know the content of free lime, which may be determined by a chemical extraction method (Section 4.3.3). The calculation is as follows:

- (1) Assume that the compositions of the four major phases are  $\text{C}_3\text{S}$ ,  $\text{C}_2\text{S}$ ,  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$ .
- (2) Assume that the  $\text{Fe}_2\text{O}_3$  occurs as  $\text{C}_4\text{AF}$ .
- (3) Assume that the remaining  $\text{Al}_2\text{O}_3$  occurs as  $\text{C}_3\text{A}$ .
- (4) Deduct from the  $\text{CaO}$  content the amounts attributable to  $\text{C}_4\text{AF}$ ,  $\text{C}_3\text{A}$  and free lime, and solve two simultaneous equations to obtain the contents of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ .

This leads to the following equations, in which  $\text{CaO}$  is assumed to have been corrected for free lime: